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Water isotopic variability in Mallorca: a path to understanding past changes in hydroclimate

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Abstract

This paper reports the first results on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of precipitations, cave drip waters, and groundwaters from sites in Mallorca (Balearic Islands, western Mediterranean), a key region for paleoclimate studies. Understanding the isotopic variability and the sources of moisture in modern climate systems is required to develop speleothem isotope-based climate reconstructions. The stable isotopic composition of precipitation was analyzed in samples collected between March 2012 and March 2013. The values are in the range reported by GNIP Palma station. Based on these results, the local meteoric water line $\delta^2\text{H} = 7.9 (\pm 0.3) \delta^{18}\text{O} + 10.8 (\pm 2.5)$ was derived, with slightly lower slope than GMWL. The results help tracking two main sources of air masses affecting the study sites: rain events with the highest $\delta^{18}\text{O}$ values ($> -5 \text{ ‰}$) originate over the Mediterranean Sea, whereas the more depleted samples ($< -8 \text{ ‰}$) are sourced in the North Atlantic region. The back trajectory analysis and deuterium excess values, ranging from 0.4 to 18.4 ‰, further support our findings. To assess the isotopic variation across the island, water samples from eight caves were collected. The $\delta^{18}\text{O}$ values range between -6.9 and -1.6 ‰ . With one exception (Artà), the isotopic composition of waters in caves located along the coast (Drac, Vallgornera, Cala Varques, Tancada, and Son Sant Martí) indicates Mediterranean-sourced moisture masses. By contrast, the drip water $\delta^{18}\text{O}$ values for inland caves (Campanet, ses Rates Pinyades) or developed under a thick ($>50 \text{ m}$) limestone cap (Artà) exhibit more negative values. A well-homogenized aquifer supplied by rainwaters of both origins is clearly indicated by groundwater $\delta^{18}\text{O}$ values, which show to be within 2.4 ‰ of the unweighted arithmetic mean of -7.4 ‰ . Although limited, the isotopic data presented here constitute the baseline for future studies using speleothem $\delta^{18}\text{O}$ records for western Mediterranean paleoclimate reconstructions.

Keywords: precipitation, cave drip water, groundwater, stable isotopes, Mallorca.

Running head: Stable isotope variability in Mallorcan waters

1. Introduction

Stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) have long been identified as valuable tracers in studying past and present hydrological cycle (Fricke and O'Neil, 1999; Darling, 2004; Gat, 2010; Genty et al., 2014; Guo et al., 2015). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of past precipitation are recorded and preserved in a variety of archives, such as ice cores, tree rings, peat, lake and deep-sea sediments, corals, or speleothems (Swart et al., 1993; Lowe and Walker, 2015). In the past two decades, the role of speleothems in paleoclimate reconstructions increased significantly (see Fairchild and Baker, 2012, and references therein).

Speleothems are cave deposits largely made of calcite or aragonite precipitated from CaCO_3 -oversaturated solutions. The oxygen in speleothems originates from rainwater falling at surface and percolating down through the soil and bedrock into the cave. Under optimal conditions (e.g., caves with no or negligible evaporation, no significant pCO_2 gradients, etc.), the $\delta^{18}\text{O}$ values in speleothems will reflect the isotopic signature of precipitation (Hendy, 1971; Lachniet, 2009; Feng et al., 2014). Thus, by measuring the stable isotope signature among other speleothem proxies (e.g., growth rate, Mg concentration, $^{87}\text{Sr}/^{86}\text{Sr}$, etc.), a wealth of paleoclimate information (e.g., precipitation source and amount, temperature, etc.) becomes available (Dorale et al., 2002; McDermott, 2004; Pape et al., 2010; Luetscher et al., 2015). Understanding the processes controlling the isotopic variability and the source of moisture in modern climate systems is required to better explain past changes recorded in cave deposits. This further helps assessing how the present day climate signal is transferred from meteoric water into speleothems, which are then used in isotope-based climate

reconstructions (Baldini et al., 2010; Polk et al., 2012; Feng et al., 2014).

The variations of $\delta^{18}\text{O}$ values in meteoric water (and in subsequently precipitated cave carbonates) are influenced by several processes occurring during moisture formation and its transport from the source zone to the cave site (Gat, 2000; Lachniet, 2009, and references therein). Among these, temperature is a key factor that controls the condensation of atmospheric water vapor, but, depending on the cave location, effects of continentality, elevation, amount, source, and ocean temperature could also be significant (Lachniet, 2009; Beddows et al., 2016). As rainwater passes through soil and epikarst (the highly-fractured carbonate bedrock immediately beneath the soil) towards the cave, its isotopic composition can change due to evaporative processes (Markowska et al., 2016). Differences in water residence times and pathways within the epikarst may also alter the initial isotopic composition of precipitation by mixing waters of various moisture sources and/or different rain events. All these factors play a major role in defining the isotopic signal of cave drip waters, which often deviates significantly from that of the original rainwater composition (Luo et al., 2013; Genty et al., 2014; Moreno et al., 2014).

The western Mediterranean basin is a key region for paleoclimate studies because it occupies a climatic transition zone influenced by both polar and subtropical air-masses (Celle-jeanton et al., 2001; Martrat et al., 2004; Frot et al., 2007; Hodge et al., 2008). Here we present the first results on stable oxygen and hydrogen isotope composition of precipitation, cave drip water, and groundwater collected from different sites in Mallorca, Balearic Islands.

Interpreting the isotopic variability of meteoric waters on this island is a challenging and complex task, considering the low amount of rainfall and its isotopic composition, which is influenced by either, or both, the cool North Atlantic Ocean and the much warmer Mediterranean Sea. This study captures representative information to address three key

problems: 1) to what extent the $\delta^{18}\text{O}$ values of rainwater in Mallorca reflect different moisture sources; 2) how similar is the isotopic composition of water in cave drips and rainfall; and 3) what is the spatial variability of drip water $\delta^{18}\text{O}$ across the Island of Mallorca and within the investigated caves.

2. Study area

The Island of Mallorca is located in the western Mediterranean (Fig. 1A), off the eastern coast of Spain (~190 km) and about 250 km north of the African continent (Fiol et al., 2005). With an area of 3640 km² (García and Servera, 2003), it is the largest landmass of the Balearic Archipelago. Mallorca has a typical Mediterranean climate, with hot, dry summers and mild, wet winters, with mean annual precipitations varying between 300 and 500 mm in southeast and 600-1200 mm along the Tramuntana Range (Kent et al., 2002; Ginés et al., 2012). The relatively low intensity, but spatially extensive winter precipitations are related to incursions of Atlantic systems, which may affect the entire island. In contrast, the warm season precipitations are far more scattered both in time and space (Sumner et al., 2001). Local moderate-to-severe thunderstorm events occur under sea-breeze conditions during the summer dry season, bringing as much as 125 mm of rain in coastal areas (Azorín-Molina et al., 2009). The weather remains warm throughout the year, with a mean annual temperature around 16-17 °C, but exceptionally it can reach 41 °C during summer and -6 °C in the winter (Ginés et al., 2012).

Previous studies conducted in the western Mediterranean showed that the isotopic composition of rainfall is mainly influenced by the variability in the source of moisture and trajectories of air masses (Fig. 1A). The vapor masses formed over the Mediterranean basin produce ¹⁸O-enriched (-4.6 ‰) rains, whereas those derived from the North Atlantic Ocean are characterized by ¹⁸O-depleted (-8.5 ‰) rains due to their longer rainout trajectory over the Iberian Peninsula and lower temperatures at the source (Celle-Jeanton et al., 2001; Díaz et

al., 2007). However, within the western Mediterranean basin there are no real boundaries between the two contrasting air masses, but rather various mixing proportions of moisture originating from these source regions.

3. Methods and sampling sites

In order to characterize the water isotopic variation in Mallorca, a total of 60 samples (33 cave drip or pool waters, 11 groundwaters, and 16 rainfalls) were collected in two different campaigns and are discussed in further detail. In all cases, 4 ml glass vials were filled to the top and capped to prevent kinetic fractionation through evaporation and kept at 4 °C until measurement time. Additionally, the vials were sealed with Parafilm. A short description of the samples type and provenance is presented below.

3.1. Rainwater samples

Except for October and November, Mallorca experiences irregular and limited rainfall events each year. This makes it difficult to collect rainwater on a monthly basis and therefore, no long-term monitoring was attempted. However, 15 samples representing single rainfall events were collected between March 2012 and March 2013 at the University of Balearic Islands, Palma campus UIB (12), Selva (2), and Alcúdia (2) (Table 1). One additional sample was collected in May 2015 from Selva (Fig. 1B, i), a village in northwestern part of the island, in the close vicinity of Campanet Cave. As suggested by the summaries of monthly meteorological data provided by NOAA (2015), the precipitation regime remained almost identical over the past 5 years.

3.2. Cave waters

Water aliquots from pools or actively dripping soda-straws were sampled from eight caves located in different geographic and geologic settings across the island (Fig. 1B). Sample

codes and locations, as well as host rock type, its age, and thickness above each cave are listed in Table 2. Additional morphological and underground climatic parameters (temperature, relative humidity (RH), and CO₂ concentration) information on Campanet, Artà, Drac, and Vallgornera caves are available in Dumitru et al. (2015). To facilitate the context of understanding the isotopic variability in the other four caves, their main characteristics are presented below.

Cova Tancada (~120 m in length), opens on the eastern side of the Alcúdia Peninsula at ~10 m above sea level (asl) (Fig. 1B, e). The cave develops in upper Jurassic limestones and consists of a series of passages and large chambers, all extremely well decorated (Hodge, 2004). Bedrock thickness on top of the cave varies between 5 and 25 m. Due to its large entrance, the cave temperature and relative humidity is heavily impacted on the first 10-15 m by the outside conditions. Except for the access passage in the largest chamber (in the inner part of the cave) where a draft is felt year around, the climatic parameters are rather constant (18.5 ± 0.2 °C and over 85 % RH).

Cova de Son Sant Martí is located in the northern part of the island, 5 km southwest of Alcúdia (Fig. 1B, g). The cave entrance to the cave is a large collapse, but a stone staircase facilitate the access down to the floor of the cave where two chapels were constructed during the 13th and 14th century. The cave passages (~120 m) are carved in lower Jurassic limestones, are poorly decorated, and are situated 15 m below the surface.

Cova de ses Rates Pinyades is a relatively complex but rather small (300 m) karst cave developed in lower Jurassic limestones, ca. 5 km east of the city of Inca (Fig. 1B, h). The entrance gives access to a collapse chamber that connects, through a tight passage, with two lower level passages disposed along a prominent subvertical fracture with a NNE-SSW orientation; these are located at depths around 20 and 40 m, respectively. The cave is poorly

decorated and the only water sample was collected immediately after the narrow passage leading to the -20 m level from the tip of a soda straw.

Cova de Cala Varques is located on the eastern coast of Mallorca, 6 km south of Coves del Drac (Fig. 1B, f). It is a short (150 m) and shallow cave (less than 10 m below the surface) that developed in upper Miocene reefal limestones and calcarenites (Gràcia et al., 2000).

Cala Varques opens at 1 m asl and ~20 m from the coast and shows a profusion of speleothem decoration. No detailed data exist on the cave microclimate; occasional temperature measurements range between 20.3 and 21 °C (± 0.2 °C).

3.3. Groundwater samples

The isotopic signature of local groundwater was investigated in four types of bottled water corresponding to the following springs: Font des Teix (FT) in Bunyola (aquifer located at –461 m below present sea level; bpsl), Font Sorda de Son Cocó (FSCC) situated in Alaró (–239 m bpsl), Font Major (FM) in Esporles (–286 m bpsl), and Font de s'Aritja (FS) in Bunyola (–474 m bpsl). All springs are hosted by Upper Triassic to Lower Jurassic limestones and dolostones (Fig. 1B). The impervious horizon consists of Keuper facies rocks (siltstones and gypsum) and basalts of Upper Triassic age (Fornós et al., 2002). Samples from shallow groundwater-fed wells in Valldemossa, Pou de Judí, Selva, and Campanet villages were also sampled for this study. In addition, two samples were recovered from a pool located in the lowermost part of Pou de Can Carro, a vertical cave reaching the local water table at ~ –40 m.

3.4. Sample analysis

Oxygen and hydrogen isotopes were measured at the Babeş-Bolyai University Stable Isotope Laboratory in Cluj-Napoca (Romania), using Cavity Ring-Down Spectroscopy (CRDS) (Berden et al., 2000; Berden and Engeln, 2009) Picarro L2130-*i* instrument and vaporizer

(used in high-precision mode) following the method described by Wassenaar et al. (2012, 2013). Internal laboratory standards were calibrated using VSMOW2 and SLAP2 international standards. All $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values obtained are expressed in per mil (‰) (Craig, 1961) and normalized to the VSMOW-SLAP scale. Measurement precision is typical < 0.025 ‰ for $\delta^{18}\text{O}$ and < 0.1 ‰ for $\delta^2\text{H}$. The reproducibility between measurements of duplicate samples is ~ 0.07 ‰ and ~ 0.17 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

3.5. Storm trajectories

To trace the origin of storms delivering precipitation to our site, we used the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) model (Draxler and Hess, 1997; 1998; Draxler, 1999; Stein et al., 2015). Back trajectories were calculated for a period of 96 hours before arrival at an altitude of 2000 m above the ground for all sampled rainfall events.

4. Results

The isotopic signature of precipitations exhibits significant variation, from -15.1 to -2.2 ‰ for $\delta^{18}\text{O}$ and from -104.8 to -8.3 ‰ for $\delta^2\text{H}$. We compared our results with the rainfall isotopic composition recorded at the closest GNIP station (IAEA/WMO, 2015). This is located in Palma de Mallorca (hereafter GNIP Palma) and monitored precipitation on a monthly basis between January 2000 and December 2010.

The $\delta^{18}\text{O}$ values of cave drip/pool waters range from -6.9 to -1.7 ‰, whereas the $\delta^2\text{H}$ values vary between -42.3 and -4.1 ‰. The most negative $\delta^{18}\text{O}$ values of the entire dataset come from *Coves de Campanet*. The drip waters collected from *Coves del Drac* showed a remarkable consistency and a restricted average compositional range of -4.7 ± 0.1 ‰ $\delta^{18}\text{O}$ and -27.2 to -24.5 ‰ $\delta^2\text{H}$. Very similar $\delta^{18}\text{O}$ values (average of -4.8 ± 0.1 ‰) were measured in *Cova des Pas de Vallgornera* and *Cova de Cala Varques*. The extent of isotopic

variability in samples from *Coves d'Artà* reaches 3.1 ‰ in $\delta^{18}\text{O}$ (−3.7 ‰ to −6.8 ‰). The most ^{18}O -enriched cave waters, with an unweighted arithmetic average value of -3.2 ± 1.1 ‰ were measured in samples from *Cova Tancada*. Only one water sample was collected from *Cova de ses Rates Pinyades* (−5.8 ‰) and *Cova de Son Sant Martí* (−5.1 ‰).

The groundwaters are within 2.4 ‰ $\delta^{18}\text{O}$ of the unweighted arithmetic mean of −7.4 ‰ (see Table 3). Except for the water samples from Pou de Judí and Pou de Can Carro, which have higher $\delta^{18}\text{O}$ values (−6.1 and −5.2 ‰, respectively), all those collected in the foothills of the Tramuntana mountains are below −7 ‰ in $\delta^{18}\text{O}$ (Table 3).

5. Discussion

We first discuss rainwater data, attempting to understand the moisture sources that potentially control the $\delta^{18}\text{O}$ composition of precipitation over Mallorca Island. Next, we interpret cave water $\delta^{18}\text{O}$ values and relate them to the available data of local precipitation to evaluate the relationship between meteoric and dripping water and to estimate the variability of $\delta^{18}\text{O}$ among different caves in the area. Finally, we examine the groundwater results and we conclude with the implications of these results for climate reconstructions using oxygen isotopes in speleothems from Mallorca.

5.1. Rainwater samples

The GNIP $\delta^{18}\text{O}$ data are graphically represented as a statistical summary through their quartiles, in the so-called box-and-whisker plot (Fig. 2). Whisker plots allow a better visualization of the variability outside the upper and lower quartiles. Beside the arithmetic mean, the plot indicates the outliers as individual points. Apart from the January 2013 samples, the $\delta^{18}\text{O}$ values of precipitations collected in this study are in the range reported by GNIP Palma station, suggesting they can be considered reliable and representative data.

Using the average isotopic composition of Mediterranean and Atlantic sources calculated by Celle-Jeanton et al. (2001), it becomes evident that the majority of rainfall on the island originates from the warm Mediterranean Sea. The two different moisture sources are also shown by the back trajectory analysis of each rainfall event, which indicates that the most ^{18}O -depleted rainwaters samples ($< -8\text{‰}$) have a North Atlantic source (Fig. 3A), whereas the highest $\delta^{18}\text{O}$ values ($> -5\text{‰}$) have a clear proximal, Mediterranean or continental origin (Fig. 3B). The exception is the rain event sampled in May 2015, which has a $\delta^{18}\text{O}$ value of -2.4‰ but the HYSPLIT trajectory indicates an Atlantic origin (Fig. 3B). However, the meteorological data along this trajectory show a minimal rainout effect, with a total of 2.2 mm of precipitation, all of which occurred within the last 26 hours before arrival. Thus, we assume that one of the main influences on the water feeding the caves located on Mallorca Island would be the source effect, due to different rainout histories.

The general relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of natural terrestrial waters is described by the Global Meteoric Water Line (GMWL), an equation originally defined by Craig (1961) as $\delta^2\text{H} = 8\delta^{18}\text{O} + 10\text{‰ SMOW}$ and later refined by Rozanski et al. (1993) as $\delta^2\text{H} = 8.17\delta^{18}\text{O} + 11.27\text{‰ VSMOW}$. Due to various climatic and/or geographic parameters, the Local Meteoric Water Line (LMWL) may differ from GMWL (both in slope and intercept values), reflecting the origin of water vapor and more complex secondary processes of re-evaporation and mixing. The LMWL for Mallorca (hereafter MaWL) was calculated based on all collected rainwater samples (see Table 1) and has a slope of $7.9 (\pm 0.3)$, slightly lower than the GMWL (Fig. 4). Although slopes lower than 8 normally indicate evaporative conditions (Clark and Fritz, 1997), the majority of our rainwater samples plot along the GMWL, suggesting they experienced insignificant evaporation (Fig. 4). From the same plot it is apparent that the GNIP Palma (slope 6.6 ± 0.2) deviates more significantly from GMWL, when compared to MaWL. A reasonable explanation for this difference may

reside in the length of sampling campaign. GNIP long-term database reflects ten years sampling period, whereas our dataset comprises only one. Thus, the GNIP record captured distinctive rainout history of air masses.

The deuterium excess (*d*-excess, or simply *d*), calculated as: $d (\text{‰}) = \delta^2\text{H} - 8 \delta^{18}\text{O}$, is another useful parameter in identifying the source of water vapor (Dansgaard, 1964; Celle-Jeanton et al., 2001; Andreo et al., 2004; Dellatre et al., 2015). Gat et al. (2003) suggest that high *d* values reflect Mediterranean Sea precipitation formed under conditions of a large humidity deficit and kinetic effects through evaporation. For this reason, *d* values around or below +10 ‰ are characteristic to Atlantic-derived precipitation, whereas values closer or above +20 ‰ indicate the Mediterranean as the predominant source of water vapor (Cruz-San Julian et al., 1992). For the entire rainwater data set from which MaWL was calculated, *d* ranges from 0.4 to 18.4 ‰; the highest values (those well above 10 ‰) likely indicate a mix source of moisture from both Atlantic and Mediterranean, with a significant component related to the latter location. Also, high *d* values may suggest an admixture of locally recycled water vapors (Aemisegger et al., 2014) with the moisture from the Mediterranean (sea breezes), which is the predominant source of summer precipitations in Mallorca. Overall, eleven out of sixteen rainwater samples plot on or slightly above the MaWL, suggesting enhanced moisture recycling and negligible evaporation of the raindrops before they reach the land surface (Andreo et al., 2004; Cruz et al., 2005). Five rainwater samples plot below MaWL exhibiting a deuterium excess of less than 10 ‰. These values are indicative of kinetic evaporation of raindrops during rainfall below the clouds in an environment in which relative humidity exceeds 85 % (Merlivat and Jouzel, 1979).

5.2. Cave water samples

To assess the transfer of $\delta^{18}\text{O}$ signal from meteoric water to cave drip waters, isotopic data of rainwater above the cave would be ideal. Since there are no rainfall data (amount, isotopes)

available strictly above any of the investigated caves, we used the isotopic composition measured in precipitations collected in Palma, which is within 60 km of our caves. The $\delta^{18}\text{O}$ values of rainwaters from Selva and Alcúdia (Fig. 1B) were used to further evaluate the isotopic signature in cave drip and groundwater samples collected within 15 km of each of these locations.

The isotopic composition of most cave waters largely overlaps the Mediterranean-sourced summer precipitation field (yellow area in Fig. 5A). Because in each cave the isotope signature of drip waters is rather distinct, they are discussed separately.

The stable isotope ratios of pool waters are similar to those of drips feeding them, suggesting that non-evaporative conditions exist within *Coves de Campanet*. This statement is supported by constant temperature ($21 \pm 0.2\text{ }^{\circ}\text{C}$) and relative humidity ($>90\%$) measured throughout the year. The $\delta^{18}\text{O}$ values range between -6.9 and -4.1 ‰ , overlapping some of the GNIP winter rainfalls. The cave waters have an unweighted arithmetic average of $-6.5 \pm 0.3\text{ ‰}$, after omitting two samples collected near the cave entrance (CAM 1, CAM 2; Table 2), which may have been affected by non-equilibrium effects. The presence of active air circulation in this section of the cave (Dumitru et al., 2015) can account for higher evaporation rates, and thus more positive values.

The amount of precipitation falling at this inland location during summer is insignificant. Consequently, most of the rainwater is more likely to be lost to evapotranspiration prior to infiltrating into the epikarst, hence, cave summer recharge is very low or absent. Instead, the increase in fall/winter precipitation correlates with an increase in recharge, when a high rate of infiltration efficiency is expected during periods of above-average precipitation. This situation has been tested in November 2012, after a 5-month long drought in the Campanet area. Following a rainy period extending from October 30 to November 28 (Table 1), most stalactites and soda straws in Campanet were active. The $\delta^{18}\text{O}$ values of samples CAM 9 to

11 collected in Sala del Llac (Table 2) within 2-3 days of two major rainfalls (October 30 and November 11) are ~2 ‰ more ^{18}O -enriched, relative to the rainwater collected in Selva, indicating very short residence time and some mixing with water stored in the vadose zone. However, if considering the average of all rainfall events recorded in the above-mentioned period, the difference is only 0.5 ‰, suggesting that an effective isotopic homogenization occurred along the vertical flow path. Thus, it is safe to assume that reactivation of dripping in Campanet beginning with November 2012 was triggered by these heavy rainfalls. Since the back trajectory analysis of all these rain events indicates an Atlantic sourced moisture (Fig. 3A), the low $\delta^{18}\text{O}$ values of Campanet waters primarily reflect the composition of precipitations originating from this region.

The difference between $\delta^{18}\text{O}$ values in coeval drip waters in *Coves del Drac* and *Cova de Cala Varques* is small (<0.7 ‰; Table 2), whereas in *Cova des Pas de Vallgornera* it shows significantly less variability, ranging between -4.9 and -4.7‰. Combining the inferences based on the narrow isotopic range and insignificant evaporative effects due to cave relative humidity exceeding 95 %, the ^{18}O -enriched cave waters imply that the majority of recharge is largely supplied by summer Mediterranean rainfall events. Considering the thin limestone cap above these caves (<10 m), we argue that the residence time of meteoric waters in epikarst is short. This assumption is further supported by the minor variability of cave drip water $\delta^{18}\text{O}$ values when compared to the meteoric precipitations feeding cave drips and pools in this part of the island.

The highest value (-3.7 ‰) in *Coves d'Artà* corresponds to a soda straw (ARW 1) from which drops were falling every 4 minutes, favoring kinetic effects due to high evaporation rates. The depletion in heavy isotope concentrations in sample ARW 2 collected from a 5 m² manmade pool may be caused by evaporation or may represent non-homogenized infiltration events. The fact that the pool is fed by over 15 stalactites that are active year around,

suggests a storage zone in the unsaturated zone above the cave, in which individual rainwater events are homogenized. Therefore, fast travel times that would promote less mixed meteoric waters are unlikely and the only process that can account for ^{18}O -enrichment in ARW 2 is evaporation.

The more negative values (-6.3 and -6.8 ‰) represent water samples collected from small pools fed by single or maximum 5 dripping points. Due to their location within the cave and thickness of limestone above (100–150 m), it is expected that samples ARW 3 and 4 are representative for drip water supplied from a well-homogenized recharge source that delivers mix waters of both Mediterranean and Atlantic origin (~ -6.5 ‰). Considering the extent of the unsaturated zone above the cave and that the bulk water rate is low and relatively constant for most drips throughout the year, it is conceivable that the residence time of meteoric waters is long enough to damp variations in the $\delta^{18}\text{O}$ values of rainfalls of various moisture sources. The oxygen isotopic composition in stalagmites formed at such locations should reflect long-term (annual or greater) paleoclimate variability at local to regional scale.

The $\delta^{18}\text{O}$ values of two rainwater samples collected in Alcúdia and drip waters from *Cova Tancada* (10 km E of this town) range between -4.2 and -1.7 ‰, falling in the Mediterranean-sourced summer precipitation field (Fig. 5A). The very high $\delta^{18}\text{O}$ value of sample CT3 (Table 2) likely reflects evaporative effects, since it was collected from a pool located near a passage constriction that causes strong ventilation in that section of the cave. The isotopic composition of the other three samples positioned near or above the MaWL, are very similar to those measured in sea breeze-related rainfalls (both in Palma and Alcúdia) delivering water from vapor that formed when relative humidity was less than ~ 85 % (Pfahl and Sodemann, 2014).

Having only one drip water sample analyzed from *Cova de Son Sant Martí* and *ses Rates Pinyades*, any discussion concerning their hydrologic system would be speculative.

However, their $\delta^{18}\text{O}$ and d -excess values combined with the rest of our isotope data provide support for the origin of the air masses feeding the drip water in caves across Mallorca Island.

In caves located very close to the coast, one may expect cave-dripping water to be a mix of rain, fog drip (Aravena et al., 1989), or seawater spray (Caballero et al., 1996). However, the $\delta^{18}\text{O}$ of the majority of our cave drip waters plot slightly above the MaWL (Fig. 5B), implying only meteoric water reaches the dripping sites. Fog is a seasonal phenomenon that is common for the central-eastern part of the island where no caves were sampled; hence its potential role as a source of water was not considered.

It is worth noting is that with one exception (Artà), the $\delta^{18}\text{O}$ of drip water sampled in caves located within 500 m from the coast, fall close to, or above the average isotopic value expected for Mediterranean sourced moisture masses (Fig. 6). Artà is a special case because of the thick vadose zone above the cave that allows for an effective isotopic homogenization of seasonal rainfall events.

The isotopic signature of water samples in caves located further inland (>10 km) approaches or overlaps the estimated $\delta^{18}\text{O}$ isotopic range (−6.9 to −6.1 ‰; Fig. 6) calculated for locations in Mallorca (0-400 m altitude) using the algorithm developed by Bowen and Revenaugh (2003). This theoretic field appears to characterize the isotopic composition of well-mixed reservoirs in the vadose zone, in which approximately equal amounts of Mediterranean and Atlantic rainfalls are homogenized. The sample from Son Sant Martí plots slightly below the average $\delta^{18}\text{O}$ value of the Mediterranean precipitations. The possible reason for the somehow more ^{18}O -depleted drip water could be the distance from the sea (1.2 km) or lesser contribution from ^{18}O -enriched rainfalls associated with sea breeze fronts.

5.3. Groundwater samples

Compared to the more scattered values of rainfalls (-15.1 and -2.2 ‰), the isotopic composition of groundwaters exhibits a narrower range of variation (Fig. 4), indicating an efficient isotopic homogenization of different rain events (Cruz et al., 2005; Onac et al., 2008; Pape et al., 2010). The d -excess ranges from 12.3 to 25.9 ‰ with a mean value of ~ 17 ‰. Also seen in Fig. 4 is that all groundwater samples are situated slightly above the GMWL and MaWL. The highest $\delta^{18}\text{O}$ values of -5.4 and -5.2 ‰ measured in *Can Carro Cave* characterize an unconfined aquifer fed by meteoric water heated at depth whereupon it rises back (Mateos et al., 2005). An enriched value (-6.1 ‰) was also measured in the water sample from Pou de Judí Well, which is very close to that of drip water collected from Rates Pinyades Cave (-5.9 ‰). Both locations are in the Inca basin, for which we infer a mix source feeding the epikarst-storage reservoir.

Taken together, the d -excess values and the isotopic data of local groundwater, suggest that the main part of Mallorca's long-term aquifers recharge is predominantly supplied by Atlantic-origin vapor masses. Fog drip has been documented to contribute to groundwater recharge (Ingraham and Matthews, 1988; Prada et al., 2015). However, all our sampled sites are lying outside the fog area known in Mallorca, therefore the input from fog drip is negligible. Without a larger isotope dataset, specific information on individual rain events, and the age of groundwater, it would be speculative to draw any further conclusions on the origin and type of precipitation events dominating recharge.

6. Conclusions

Our work adds new information on isotopic variability of meteoric precipitation, drip water, and groundwater from Mallorca, a potential key site for speleothem-based paleoclimatic and sea-level reconstructions.

The MaWL ($\delta^2\text{H} = 7.9 \delta^{18}\text{O} + 10.8$) constructed on the basis of a year-long sampling of individual rainfall events is much closer to the GMWL compared to the one generated using the GNIP Palma database ($\delta^2\text{H} = 6.6 \delta^{18}\text{O} + 1.7$). The lower slope of the GNIP Palma meteoric water line probably reflects the much longer sampling interval that averages the effects of storms originating in different source areas and some small differences in evaporative isotope fractionation of H and O, respectively.

In this study, five out of eight caves are located within 0.5 km of the coastline (Fig. 1B). Four samples plot to the right of MaWL, pointing out they may have experienced evaporation prior to percolating through the thin soil and epikarst zone. The samples above MaWL may originate from rainfalls enriched due to enhanced ocean moisture recycling.

The data available for this study are clearly insufficient to explain conclusively the observed isotopic spatially variability across the island of Mallorca or within the caves. However, collectively, the $\delta^{18}\text{O}$ values of precipitations, which are in the range of GNIP data, and those of cave drip water help tracking two main origins of air masses affecting the study sites. The enriched ^{18}O values and d -excess >10 ‰ of drip waters in Drac, Vallgornera, Cala Varques, Tancada, and Son Sant Martí caves indicate vapor masses of Mediterranean origin, likely related to local thunderstorms developed along the sea-breeze fronts. The more ^{18}O -depleted values measured in Campanet, ses Rates Pinyades, and parts of the Artà caves may reflect a dominant contribution from rains of Atlantic source area. Different mixing, evaporation rates, and flow pathways within the epikarst may also impact the final isotopic composition, however, no recharge data are available to assess the role of these processes.

The spatial pattern of cave drip $\delta^{18}\text{O}$ values across Mallorca can be primarily attributed to the source area (Mediterranean vs. Atlantic) of the water vapor in the rain bearing clouds. In addition, the amount of rainfall per event, frontal depressions vs. convective storms, evaporation, and moisture recycling could also cause this range of $\delta^{18}\text{O}$ values. As for the

$\delta^{18}\text{O}$ variability within Campanet, Tancada, and Artà caves, for which four or more samples were analyzed, the following factors might be responsible: i) thickness of the bedrock above the cave, which controls water residence time and thus the degree of isotopic homogenization, and ii) particular cave climatic conditions (i.e., relative humidity, temperature, and ventilation). Any of these physical drivers can potentially modify the $\delta^{18}\text{O}$ values of drip water at a specific location within the cave.

Oxygen and hydrogen isotopes in rainfall and drip water are key to understanding past variability of moisture sources. It is expected that speleothems from inland caves and/or those having a thick vadose zone above them are ideal for reconstructing annual or greater scale variations in western Mediterranean paleoclimate. The isotopic composition of drip water from such caves likely reflects predominantly Atlantic sourced moisture. In contrast, speleothem paleoclimate records from caves along the coast having a thin limestone cap and thus fast recharge to drip sites will likely provide a seasonal signal associated with precipitations generated by moisture masses that originate from the Mediterranean.

This dataset constitutes the baseline for future studies aiming to assist speleothem-based paleoclimate reconstructions in the western Mediterranean basin.

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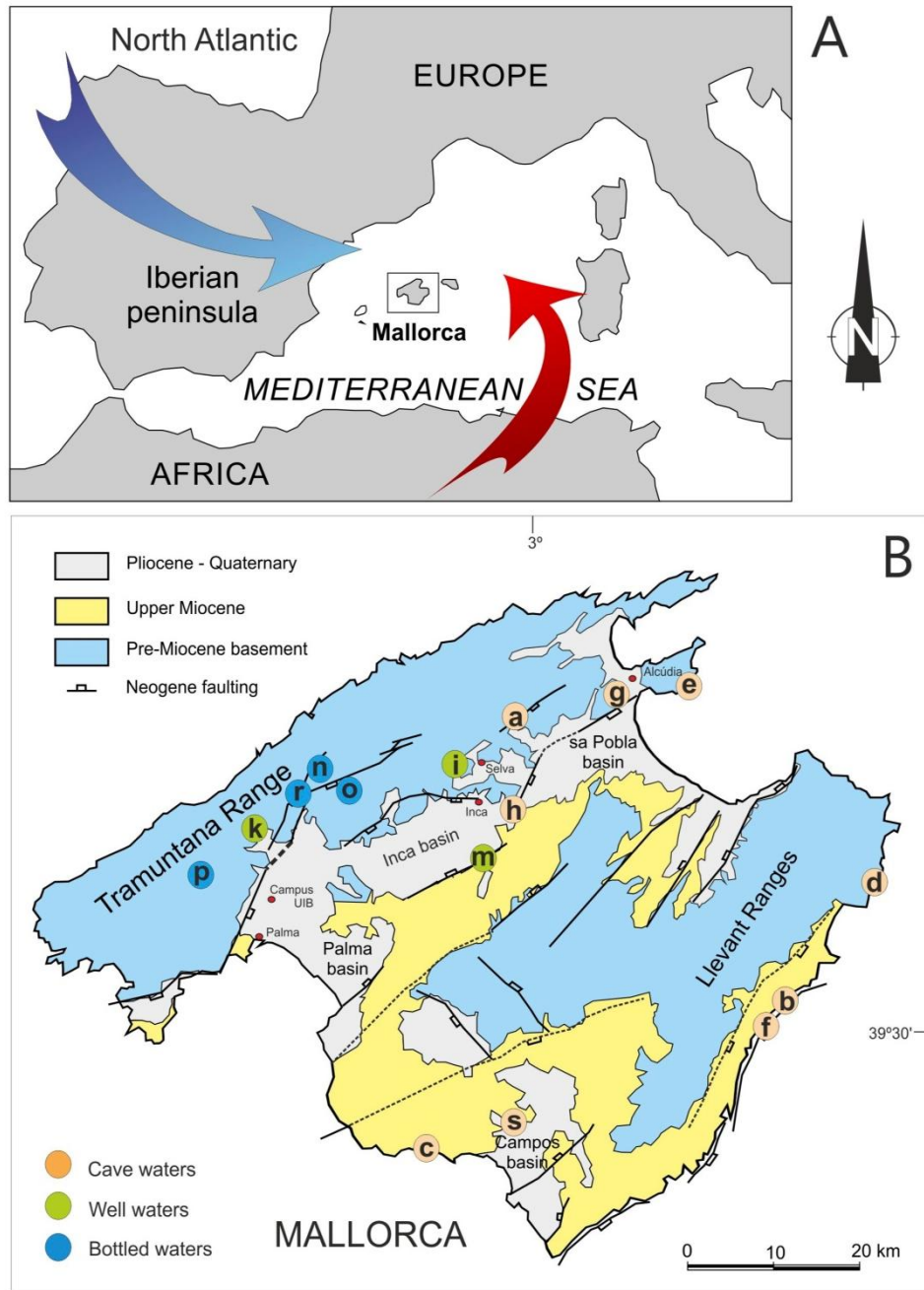


Fig. 1. A) Map showing the main trajectories of air masses affecting the western Mediterranean; B) sampling sites locations: a - Coves de Campanet; b - Coves del Drac; c - Cova des Pas de Vallgornera; d - Coves d'Artà; e - Cova Tancada; f - Cova de Cala Varques; g - Cova de Son Sant Martí; h -Cova de ses Rates Pinyades; i - Selva; k - Valldemossa, m - Pou de Judí, n - Font des Teix, o - Font Sorda de Son Cocó, p - Font Major, r - Font de s'Aritja, s - Pou de Can Carro.

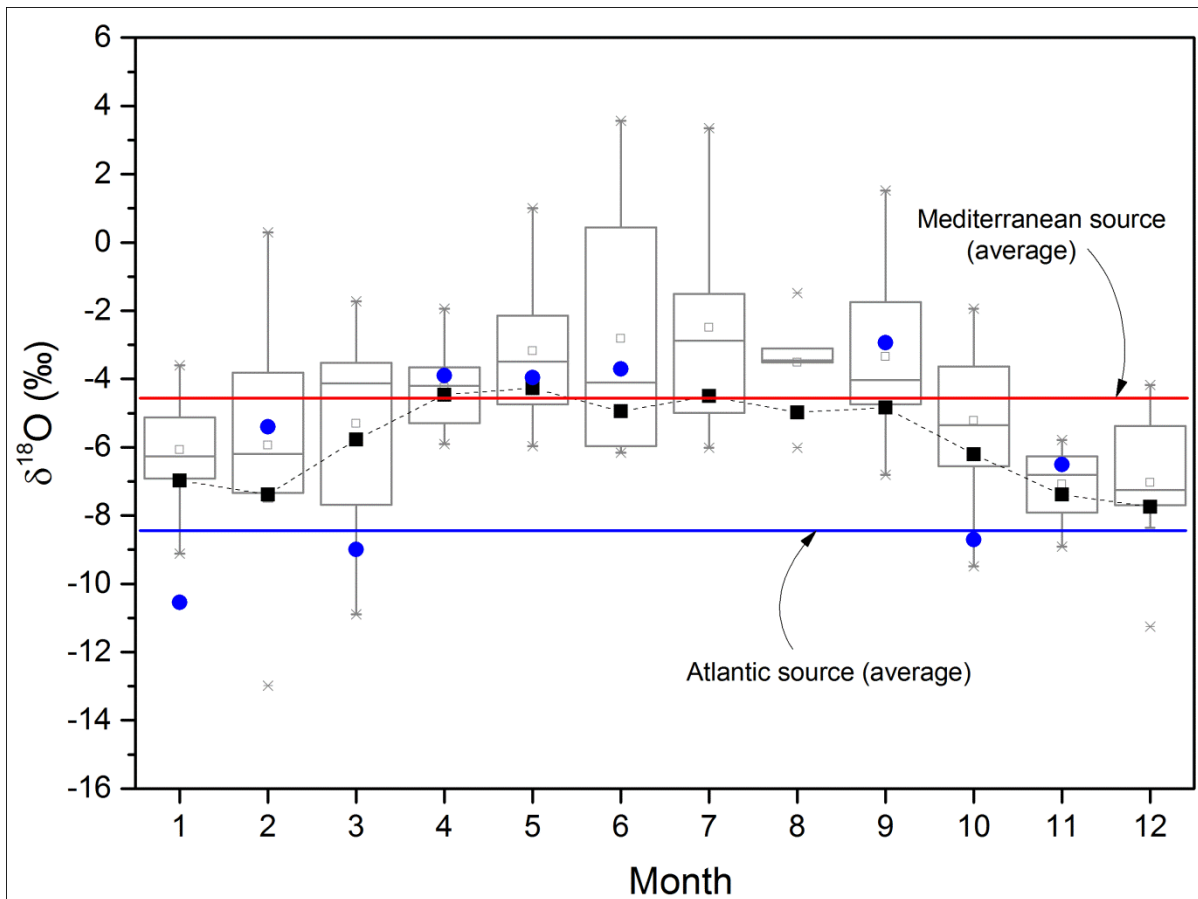


Fig. 2. Box-and-whisker plot of $\delta^{18}\text{O}$ GNIP Palma (solid/open square: weighted/unweighted mean isotope value; IAEA/WMO, 2015) and this study (solid blue dots) precipitation data. Red and blue horizontal lines represent the average isotopic value for Mediterranean- and Atlantic-source precipitations, respectively.

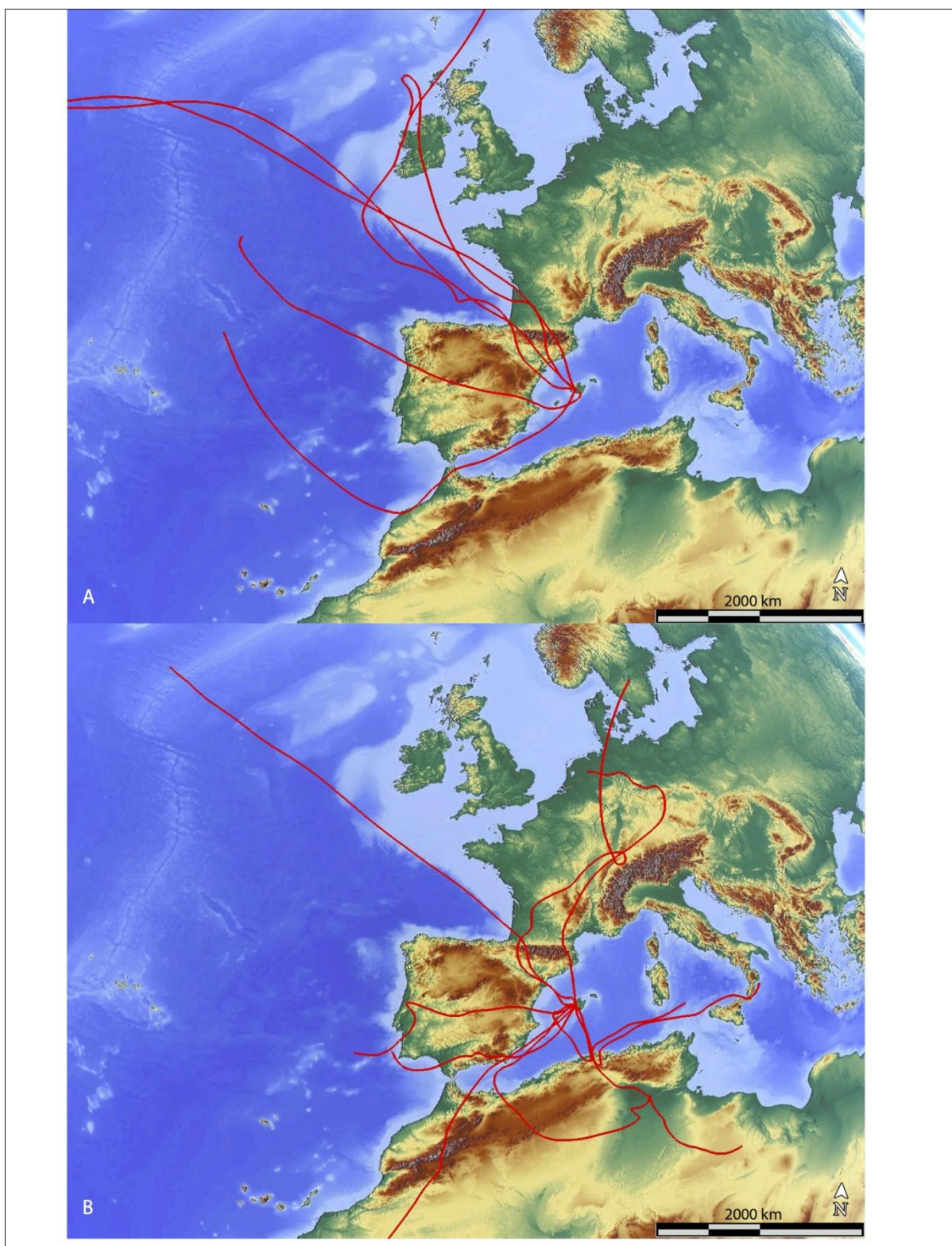


Fig. 3. HYSPLIT back trajectories for rainwater samples with the lowest (A) and highest (B) $\delta^{18}\text{O}$ values.

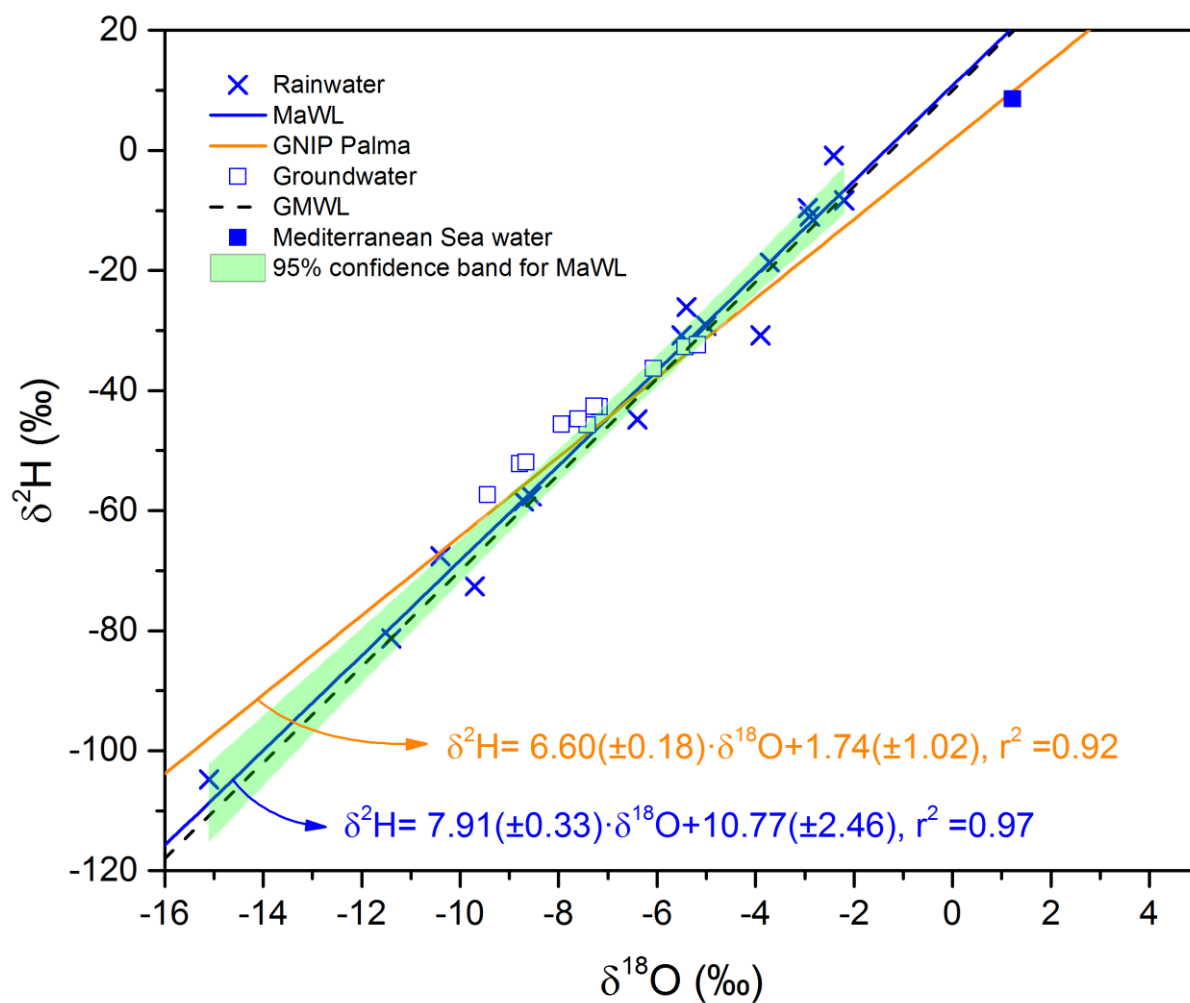


Fig. 4. The relationship between GMWL (dashed line) and the local meteoric water lines constructed based on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation from GNIP Palma (orange) and this study (blue). Also plotted are groundwaters samples (open blue squares).

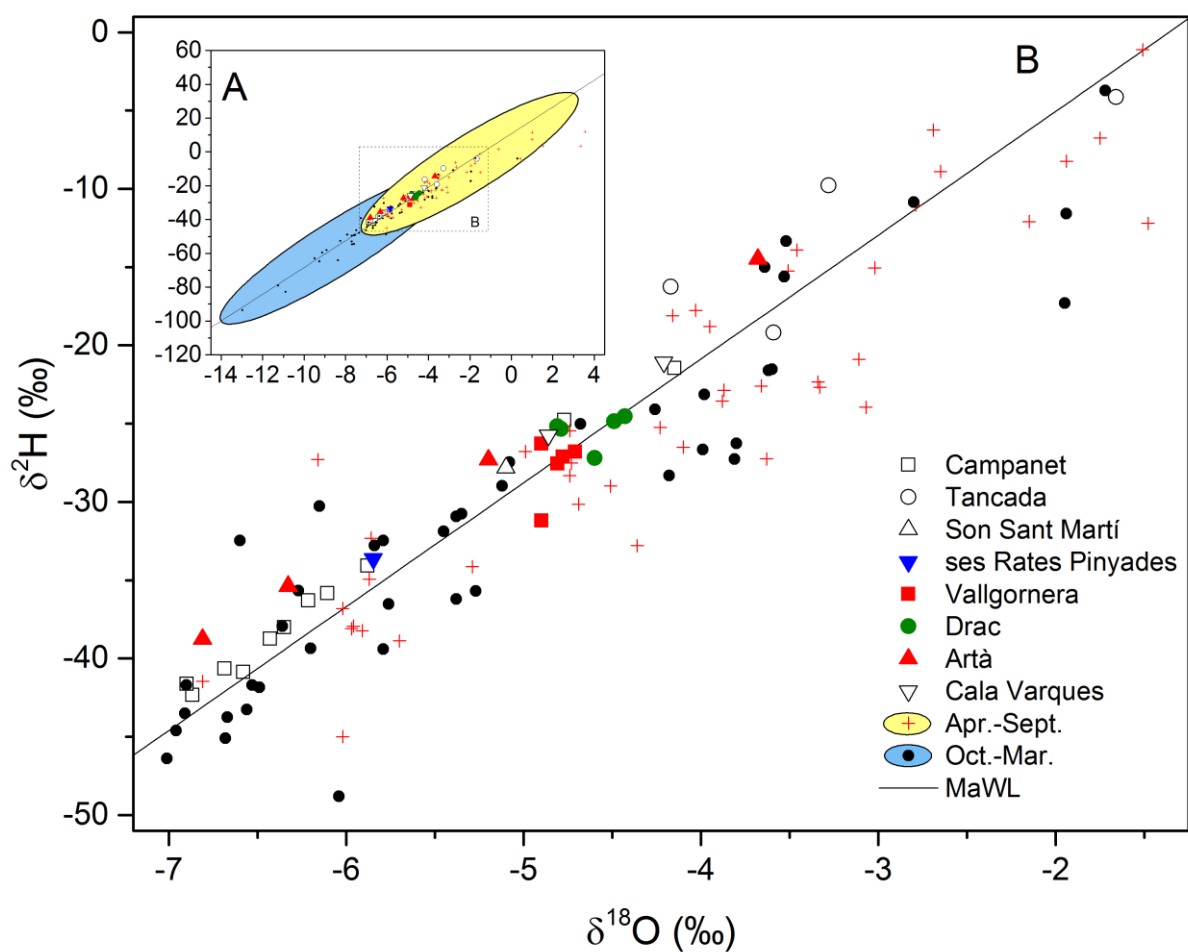


Fig. 5. A) Isotopic composition of drip/pool water samples from eight caves (this study) along with GNIP Palma precipitation (yellow: summer; blue: winter); B) Close up showing the isotopic composition of each cave water sample. MaWL is represented by solid black line.

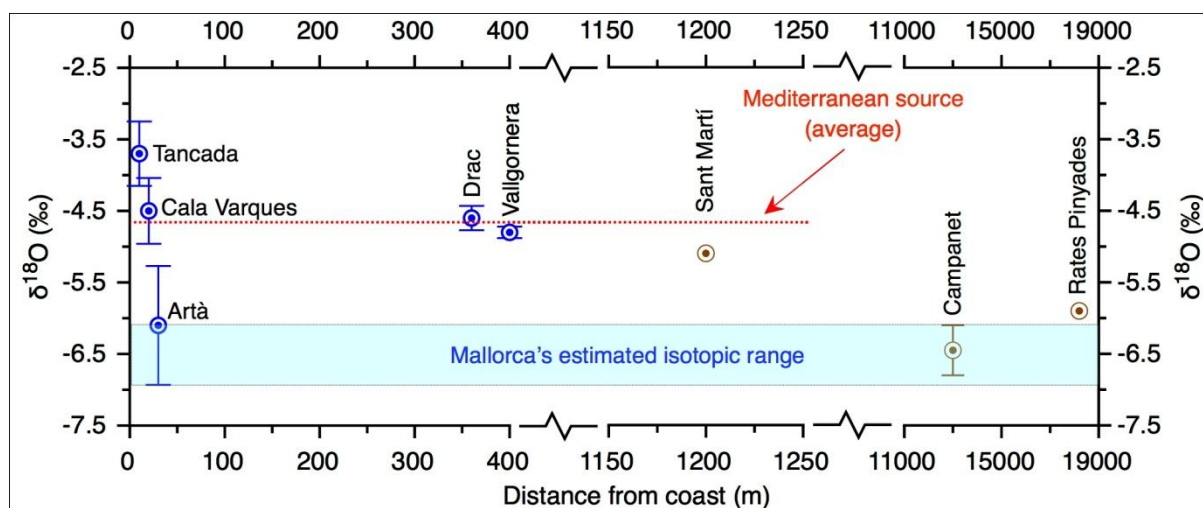


Fig. 6. Mean cave drip water $\delta^{18}\text{O}$ values versus distance from the Mediterranean Sea coast. Shaded rectangle encompasses the estimated isotopic range for Mallorca (see text for details).

Table 1. Isotopic data of precipitations collected in Palma campus UIB, Selva, and Alcúdia.

Meteoric precipitation (sampling date and location)	$\delta^{18}\text{O}$ (‰)	<i>d</i>-excess (‰)
March 20, 2012	-2.9	12.20
April 5, 2012	-3.9	0.40
May 1, 2012	-5.5	13.20
June 3, 2012 (Alcúdia)	-3.71	18.37
September 2, 2012 (Alcúdia)	-2.94	16.46
October 30, 2012 (Selva)	-8.71	11.26
November 10, 2012	-2.2	9.30
November 11, 2012 (Selva)	-8.55	11.50
November 17, 2012	-6.4	6.40
November 18, 2012	-5	10.80
November 28, 2012	-10.4	15.60
January 24, 2013	-11.4	9.90
January 28, 2013	-9.7	5.00
February 23, 2013	-5.4	17.10
March 13, 2013	-15.1	16.00
May 22, 2015 (Selva)	-2.41	18.42

Table 2. List of investigated caves, their geologic setting, and isotopic data.

Location	Station name	Sampling site	Host rock age and thickness above cave	$\delta^{18}\text{O}$ (‰)	d -excess (‰)
Coves de Campanet	CAM 1	Pool in Sala Romàntica	Upper Triassic dolostone (5 - 20 m)	-4.15	11.77
	CAM 2	Soda straw above pool in Sala Romàntica		-4.77	13.41
	CAM 3	Dripping point, left side of Sala Romàntica		-6.87	12.60
	CAM 4	Soda straw, right side of Sala Romàntica		-5.88	12.95
	CAM 5	Soda straw, left passage towards Sala del Llac		-6.11	13.01
	CAM 6	Pool in Sala del Llac		-6.69	12.87
	CAM 7	Soda straw at the end of Sala del Llac		-6.21	13.43
	CAM 8	Soda straw between Sala del Llac and Palmera		-6.90	13.57
	CAM 9	Small pool in Sala del Llac		-6.43	10.10
	CAM 10	Large pool in Sala del Llac		-6.35	10.67
	CAM 11	Soda straw at the end of Sala del Llac		-6.58	11.78
Coves del Drac	Drac 1	Soda straws in Cova Blanca	Upper Miocene limestone (15 m)	-4.60	9.60
	Drac 2			-4.81	20.24
	Drac 3			-4.43	23.96
	Drac 4			-4.79	20.68
	Drac 5			-4.49	21.51
Cova des Pas de Vallgornera	VLG 1	Soda straws in the Entrance Room	Upper Miocene limestone (10 m)	-4.90	8.00
	VLG-2			-4.90	22.62
	VLG-3	Pool Sector Nord		-4.81	22.80
	VLG-4	Soda straw Sector N		-4.71	22.18
	VLG -5	Soda straw Sector F		-4.78	22.13
Coves d'Artà	ARW 1	Soda straw between Inferno and Purgatorio	Middle Jurassic limestone (20 - 150 m)	-3.68	14.97
	ARW 2	Manmade water pool near Inferno		-5.20	14.29
	ARW 3	Pool on the right side descending from "Heaven"		-6.81	15.72
	ARW 4	Small pool on a dome before exiting the cave		-6.33	15.25
Cova Tancada	CT 1	Soda straw in the first chamber, near entrance	Lower Jurassic limestone (5 - 30 m)	-3.59	9.53
	CT 2	Soda straw before entering the big chamber		-4.17	17.10
	CT 3	Pool at the entrance in the big chamber (left side)		-1.66	9.15
	CT 4	Soda straw at the far end of the big chamber		-3.28	16.46
Cova de Cala Varques	CVB 1	Soda straw right after constricted passage	Upper Miocene limestone (5 m)	-4.21	12.60
	CVB 2	Soda straw in the upper part of second chamber		-4.86	13.13
Cova de Son Sant Martí	CSM	Soda straw near the end of the stairs	Lower Jurassic limestone (15 m)	-5.10	12.99
Cova de ses Rates Pinyades	RPC	Soda straw before the vertical passage	Lower Jurassic limestone (20 m)	-5.85	13.16

Table 3. Isotopic data of groundwaters.

Groundwater sampling location	$\delta^{18}\text{O}$ (‰)	<i>d</i>-excess (‰)
Campanet	-7.42	13.60
Font des Teix	-8.79	18.14
Font Sorda de Son Cocó	-7.17	14.66
Font Major	-9.44	18.19
Font de s'Aritja	-8.66	17.37
Selva	-7.28	15.59
Pou de Judí	-6.08	12.27
Valldemossa (1)	-7.60	16.10
Valldemossa (2)	-7.94	17.95
Can Carro (1)	-5.43	25.96
Can Carro (2)	-5.18	24.26